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STATE OF THE ART AND CERTAIN NEW DEVELOPMENTS IN THE MOLECULAR BEAM METHOD

V. B. Leonas

1. Introduction

The term "molecular beam" is applied to a space-localized stream of particles flying parallel to one another without interacting, with no distinction being made between atoms and molecules, and only one concept being used.

The molecular beam method (MBM) is based on the fact that the beam, formed in some manner, becomes the object of an investigation either immediately after reception or after being acted upon. Whereas in the former case the particles of the beam "carry" information on the thermodynamic and physicochemical state in the formation region of the beam, in the latter case information can be obtained on the reaction of the particles forming the beam to this influence. The methods of exerting an influence on the particles of the beam are diverse: exposure to light, reflection from the surface of a solid, intersection with a perpendicular beam, passage across a magnetic field, etc.

Since in the limiting case it is possible to record individual particles of the beam, it is obvious that the MBM permits experiments on the level of a single elementary event. The advantages of the method do not end here, however. In most cases, the experiment records an indirect effect which is not masked by side phenomena, and the interpretation of the data obtained is thus considerably simplified.

A convincing illustration of the extensive applications of the MBM is the very incomplete list of problems which have already been solved or are being solved by this method.[1]

1. The first works relating to this method were devoted to problems involved in the substantiation of the theory of gases.

2. The method has found an ideal application in fundamental problems involved in demonstrating the wave nature of particles.

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[1]A detailed bibliography of works published prior to 1955 is given in Ref. 1.

3. It has found very extensive application in works devoted to precision measurements of the electric and magnetic moments of atoms and molecules, spin and magnetic moments of nuclei, and the study of microwave spectra of molecules and atoms.

4. The use of this method in the study of the effective scattering cross sections of molecular collisions has proven fruitful. On the basis of these measurements, valuable information has been obtained on the /288 force fields of molecules and atoms both in the field of pure repulsion and in pure attraction.

5. The MBM is also perhaps the most convenient means of solving a group of problems involved in the interaction of molecules and atoms with the surface of a solid. The current importance of these investigations is evident in connection with the requirements of modern technology.

6. The MBM in combination with mass analysis is the most effective means of obtaining information on the thermodynamic and physicochemical state of matter at high temperatures.

7. In concluding this incomplete list, we should mention that molecular beams can be used in plasma investigations. This is one of the vital elements of quantum amplifiers and generators and of ion sources for the injection of particles into accelerators and devices for the achievement of thermonuclear fusion.

In practice, in the majority of the above-mentioned studies, the decisive factor determining their success is the problem of the beam intensity. The finer the effect being studied, the higher should be the intensity, which should be treated in a broader sense than the useful signal to noise ratio.

For this reason, two lines of research are possible in experimental work: on the one hand, the direct increase of the beam intensity, and on the other, the improvement of the recording facilities, i.e., a more efficient use of the signal received. Both methods are equivalent in their results, but the optimum one should of course be selected for each individual case.

In the present article, it would be desirable to try to give a more or less complete description of the numerous designs and individual problems encountered in practical work with molecular beams. This end will be served much better by the original works; here we shall emphasize only the fundamental principles of the experimental devices. An analogous situation is also encountered when the various applications of the MBM are considered. We shall present only the main outlines of these applications.

In the exposition which follows, consideration is given to the methods of creating and recording molecular beams, and also to a series of applications of the MBM to the solution of specific problems in molecular and chemical physics. Taking into account the presence of Refs. 1-5, we shall of course attempt to avoid touching upon questions which have been thoroughly treated in these works.

2. THE MBM TECHNIQUE (METHODS OF CREATING, RECORDING, AND SELECTING BEAMS

1. The "furnace" method. The classical "furnace" method, first used by Dunoyer (Ref. 6), was brought to instrumental perfection by Stern.[1] A diagram of the furnace or effusion source is shown in Figure 1a. A source of this type has been in wide use up to the present time; beams of a large number of elements of the periodic table and chemical compounds have been obtained by this method (Ref. 4). The advantage of this molecular beam source, which is described in detail in many works (Refs. 1-3), is the possibility of calculating the beam intensity from the known geometry of the source. Its drawback is the impossibility of obtaining high velocities and intensities in the collimated beam (i.e., the impossibility of obtaining beams of high particle flux density). /289

Thus, in Ref. 8, beams with a high intensity, of the order of 10^{17} molecules/cm^2 sec, have been obtained by raising the evacuating capacity considerably, but then the cross section of the beam at a distance of only 4 cm from the exit aperture was 4·8 mm^2.

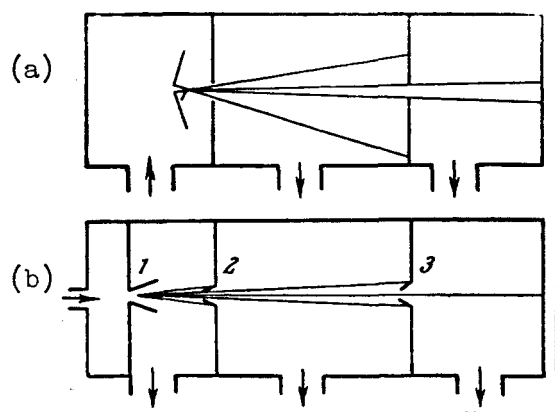

Figure 1. Schematic representation of sources of the furnace (a) and gas-dynamical (b) type
1-Nozzle; 2, 3-conical slits.

[1]A detailed bibliography of Stern's works may be found in Ref. 7.

Substantial improvements of furnace-type sources were due to the use of separate long tubes (Ref. 9) and a "packet" arrangement proposed in Ref. 4. A schematic representation of such a multichannel source is shown in Figure 2a; an experimental angular distribution of the intensity for this source is shown in the same figure (Figure 2b) (Ref. 10).

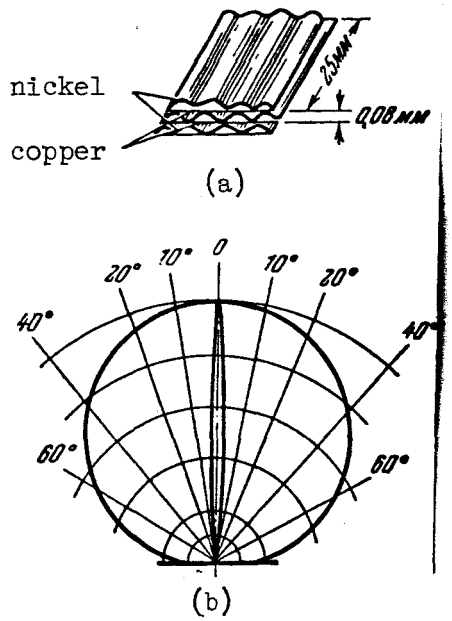

Figure 2. Structure of a multichannel source (a) and angular intensity distribution (Ref. 10) for this source (b). The circle shows the intensity diagram corresponding to the usual effusion source.

Multichannel sources of various designs have been studied and used by several authors (Refs. 10-13). A detailed theoretical treatment of the characteristics (intensity, directivity diagram) of such sources, but without consideration of the mutual influence of the individual beams, is given in Refs. 14-16. In particular, Troitskiy (Ref. 16) has developed a general method of calculating directivity diagrams and beam intensities.

For multichannel sources, the restriction on the energy of the beam particles is of course preserved, since the particle velocities are determined by the temperature, which cannot be raised considerably.

One of the successful construction methods used for their preparation is the one proposed in Ref. 11, involving the electrolytic etching of thin (20μ) wires collected together in a polymerizable plastic. The

number of channels can thus be raised to $530/mm^2$, and the "transparency", to 65 percent. The practical advantages of using multichannel sources may be illustrated as follows: in Ref. 10, at a distance of 40 cm from the source and a pressure of 10^{-5} mm Hg, it was possible to obtain a beam (N_2, H_2) with a current density of 10^{15} molecules/cm^2 sec, and this pressure was maintained by a pump with a capacity of 100 l/sec. Use of an ordinary effusion source would require a pump with a capacity of 10,000 l/sec to achieve the same results. It may be noted that in addition to an important technical application (maser), multichannel sources are of great value as gas targets of high density. /290

2. Gas-dynamical source. This source, proposed by Kantrowitz (Ref. 17), has been under intensive development in recent years, and is finding ever wider applications (Refs. 18-20). In this very ingenious method, the effusion "furnace" of the classical source is replaced by an ultrasonic jet of gas of low density (see Figure 1b). A gradual expansion of this jet brings about its conversion into a stream of molecules, i.e., a beam. The application of mass motion causes a narrowing of the diagram, analogous to that shown in Figure 2b; this makes it possible to retain a considerably greater number of particles in the beam during the collimation, and to obtain a gain in intensity as compared to the classical furnace source.

In a gas-dynamical source, in contrast to the classical source, the beam is formed in a region where the distribution of the directions of the velocity vectors, owing to the application of mass motion, differs from the distribution in free space. It appears possible to express this effect analytically and, by making the calculations, to compare the intensity of the gas-dynamical (I_{gd}) and effusion sources (I_{eff}) under the same conditions. It can be shown that the intensity achieved by the gas-dynamical molecular beam source is expressed in the form (using standard symbols)

$$I_{gd} = I_{eff} \frac{\left(1+\frac{\gamma}{2}M^2\right)\sqrt{\frac{\pi\gamma}{2}}M\left[1+\operatorname{erf}\sqrt{\frac{\gamma}{2}}M+\exp\left(-\frac{\gamma}{2}M^2\right)+\frac{1}{2}\sqrt{\frac{\pi\gamma}{2}}M\right]}{\sqrt{1+\frac{\gamma-1}{2}M^2}}$$

The results of calculations for different values of Mach numbers M are given in Table I.

The data of this table, confirmed also by direct measurements (Refs. 18, 19), characterize precisely the efficiency of a gas-dynamical source.

Table I

M	1	2	4	6	10
I_{gd}/I_{eff}	4	18	70	152	475

In experimental practice, M numbers between 4 and 6 are readily achieved, and for this reason the intensity of a gas-dynamical source is found to be two orders of magnitude greater than that of an effusion source of the same size. In order to describe a source fully, it is necessary to know the nature of the distribution and the values of the velocities in the beam. The distribution function can be written if we take into consideration the motion and expansion of the gas jet; Figure 3 shows calculated distribution curves corresponding to the different M numbers. As is evident from this figure (and confirmed by direct measurements), a substantial shift toward an increase takes place in the beam obtained from a gas-dynamical source; curve M = 0 corresponds to a classical source.

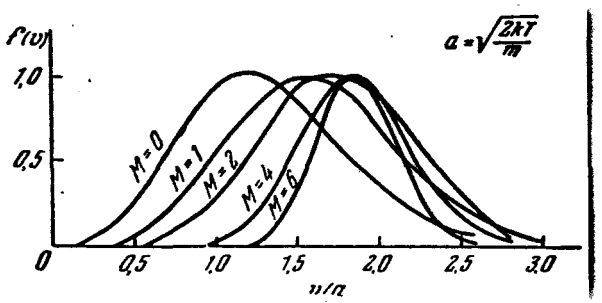

Figure 3. Velocity distribution curves of molecules of a beam produced by a gas-dynamical source for different values of the M number
The curve M = 0 corresponds to an ordinary effusion source.

Thus, by using this source, it is possible to reach an equivalent three- to fourfold increase in the initial "temperature" without heating. Preheating can provide still higher velocities. Another feature of the /291 distribution (see Figure 3) is a narrowing of the curve with an increase in the M-monoenergetization of the beam particles; this is of great technical value, since it decreases the loss of particles when mechanical selectors are employed. The design of the source may be represented as in Figure 1b. A supersonic jet of rarefied gas (pressure: 20-50 mm Hg) is created by a convergent-divergent nozzle 1, whose nozzle diameter, determined by the capacity of the pumping system, is of the order of 0.5 mm. The operation of the nozzle under these conditions can scarcely correspond to the calculated conditions, as is partly indicated by the results of Ref. 21. In the latter, the nozzle was only a convergent one,

while the divergent part was apparently formed by the boundary layer. As was shown by the measurements, no appreciable intensity loss was observed, and this result simplifies considerably the task of preparing nozzles for gas-dynamical sources. Forming slit 2, in the shape of a frustum of a cone, has very sharp edges to prevent the formation of compression shocks on them; the last slit, 3, is of the same shape. All the chambers are evacuated independently with powerful pumps. A detailed description of the vacuum part and design characteristics of such sources may be found in Refs. 18-21. The intensity and velocity of the beam obtained by a gas-dynamical source may be increased considerably when mixtures are used as the working gases. A more thorough discussion of this effect is given below in the description of the separation of gas mixtures.

A sharp increase in the intensity of the beam obtained was also observed (Refs. 22, 23) when highly cooled gases were employed: the intensity increased by two orders of magnitude, reaching $6 \cdot 10^{19}$ molecules/cm^2 sec for hydrogen. These results will be examined in somewhat greater detail below.

3. Sources with charge transfer. A widely used type of source of beam particles having high velocities is the source with charge transfer (Refs. 24-26). In this source, the ion beam, obtained by some method, undergoes a charge transfer upon passing either through a neutral gas (Refs. 24-26), or through an electron cloud (Ref. 25). A major advantage of such a source is the possibility of electric control of the ion beam, and hence, the neutral beam obtained after the charge transfer (modulation, focusing, acceleration--deceleration).

In creating a source with charge transfer it is necessary to solve two fundamental problems: choice of the type of the ion source and choice of the method of charge transfer for the ions. An analysis of these problems is beyond the scope of this discussion. We shall point out, however, one method which in our opinion is promising, and which makes it possible to create a simple ion source of high intensity, based on a hollow cathode that provides for a density of the ionizing electron current of up to 25 a/cm^2 (Ref. 27). Practically, the first sources with charge transfer were the devices described in Refs. 24 and 25. The work of Simonenko (Ref. 25) describes a source with an intensity about 100 /292 times greater than that of an effusion source of the same geometrical dimensions. An interesting feature of this device is the fact that an attempt was made to use the charge transfer in an electron cloud. It was possible to determine that for an effective neutralization, the density of the electron current should be approximately 1000 times greater

than the density of the ion beam current, which is quite feasible. Unfortunately, this work which was not pursued, involved an error. The cross sections of the ion-electron recombination were unreasonably large for the efficiency of charge transfer achieved. The latter was controlled by attenuating the current to the collector; however, this attenuation could apparently have taken place via the compensation by the current of the entrained electrons.

In Ref. 24, the beam, obtained by withdrawing the ions from the region of the glow discharge, was neutralized in a special chamber in collisions with the gas and the walls. A drawback of both of these sources is the uncertainty of the composition; however, it can be eliminated by introducing a mass analyzer between the source and the charge-transfer chamber, as for example in Ref. 28.

Another disadvantage of these devices is the impossibility of obtaining directly intense monoenergetic beams with energies in the range of 1 to 20 ev, which is of greatest interest from the practical standpoint.

As we know, the formation of ion beams of high intensity and low energies may be hindered by the space-charge effect. For this reason, a device designed to form intense (10^{18} molecules/cm^2 sec) molecular beams with velocities from 10 to 30 km/sec (Ref. 29) is particularly interesting.

A line diagram of the device is shown in Figure 4, and the beam is formed as follows: a supersonic nozzle 1 continuing as a cylindrical tube creates a stream of gas which, upon passing through it, is ionized by a high-frequency electrodeless discharge (frequency: 10-150 Mc). Then, the cylindrically symmetrical jet of the partially (10 percent) ionized gas enters the field of a sector-shaped magnet 3, which deflects the heavy charged particles (ions) by 90°. In addition to the deflection, the magnet performs the monochromatization of the velocities and the selection by masses. The neutral component of the jet falls directly into the pump entrance, and the electrons are carried away through the grounded pole pieces of the magnet. The velocity of the deflected ions is about 2 km/sec, and they are accelerated in accelerator tube 4 to the necessary velocity. The beam of neutral particles is obtained by charge exchange with the ion beam in the supersonic jet 5, which escapes into the vacuum. The separation of the ions and neutral particles is achieved by the sector-shaped magnet 6, after which the intense beam of neutral particles enters working section 7. Evacuation is accomplished by powerful diffusion pumps with the use of additional freezing.

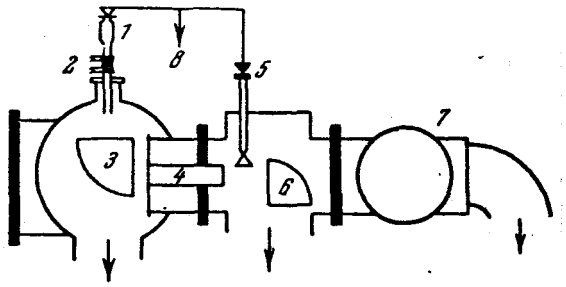

Figure 4. Schematic representation of a source producing an intense beam of fast particles (Ref. 29)
1-Nozzle extending into a tube; 2-induction coil of an SHF generator; 3-sector-shaped magnet for turning the trajectory of the ions by 90°; 4-ion accelerator; 5-nozzle forming a gas target for charge exchange with ions; 6-sector-shaped magnet for deflecting the nondischarged ions; 7-working space; 8-supply of working gas.

A source of this design is useful in problems concerning the interaction of molecules with the surface of a solid. /293

Sources with charge transfer can of course create intense beams, chiefly beams of gases and readily vaporizing substances, but the relative ease of the recording of particles with energies above 100 ev makes it possible to work with beams of low intensity. In Ref. 26 a source producing a beam of molecular nitrogen with an intensity of 10^8 to 10^{10} molecules/sec and in the range of energies between 5 and 1000 ev, respectively, is described.

4. Source with atomization. A source of intense beams of metal atoms in the range of 1 to 10 ev can be constructed on the basis of the phenomenon of directed atomization of atoms, discovered relatively recently. Wehner (Ref. 30), then several other authors (Ref. 31) observed that the atomization of single-crystal samples by fast ions occurs anisotropically, i.e., the atomized atoms move predominantly in directions which coincide with the directions of the close packing in the crystal. Measurements of the energies of the dislodged atoms, carried out in Refs. 31 and 33, showed that their values were of the order of 10 ev and higher.

On the basis of the data on the efficiency of the atomization, Wehner (Ref. 30) concluded that beams with a density of 10^{17} atoms/cm^2 sec can thus be readily obtained. A source of this type makes it possible to obtain beams of practically any metal atoms with a controllable and adjustable density; this being very advantageous when such beams are used as targets.

The directed escape of atoms was also observed (Ref. 34) when foil (Au) was bombarded with fast protons. Thus far, despite obvious advantages, this method has not been used. It should be noted that the degree of homogeneity of the velocities of atoms in such beams has not yet been sufficiently studied.

5. Molecular "catapult". A simple and original method of obtaining modulated beams is described in Ref. 35. The principle of the method (Figure 5) is based on the "catapulting" of particles by a vane rotating rapidly about an axis. This method is a form of vane radiometer in reverse. To produce the beam, the vane is placed in a space filled with gas at 10^{-4} to 10^{-3} mm Hg. The randomly moving particles, upon colliding with the surface of the rotating vane, acquire a velocity whose magnitude is related in a definite manner to the linear velocity of the vane; depending upon the nature of the reflection (inelastic, elastic), the velocity will be either close to linear, or close to twice the linear. If the working gas is one of high molecular weight, there is a possibility of effectively increasing the energy of the beam particles (up to an energy of ~1 ev).

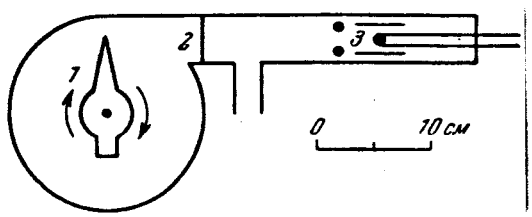

Figure 5. Diagram of a "catapult" source (Ref. 35)
1-Vane rotating at a high rate; 2-collimating slit;
3-detector.

Calculations show that for a working pressure of 10^{-3} mm Hg and a linear velocity of the vane of the order of 10^5 cm/sec, 1 cm^2 of the vane imparts a momentum of approximately 1 mg of gas (Hg) per second (i.e., approximately 10^{19} molecules/sec). Therefore, by using the method of ordinary collimation, it is possible to produce a beam whose intensity will be no less than that corresponding to an effusion source. However, in contrast to the latter, the intensity is already modulated, and this /294 is of undeniable value in detection. A source of this type may be modified by applying a readily vaporizable substance on the surface of the vane. Thus far, such sources have found only limited applications (Ref. 36).

6. Pulsed sources of molecular beams. A very convenient means for producing beams of metal atoms may prove to be the electric explosion of fine wires in a vacuum (Ref. 37). The cloud of high-temperature metal vapor (several tens of thousands of degrees) is a type of pulse-action "furnace". This method obviously presupposes the production of high-intensity beams, but it is necessary to explain the degree of homogeneity of the particles with respect to the velocities. Somewhat modified, this method was used as a source of plasma discharged and accelerated in a vacuum (Refs. 38, 39).

Another powerful source of fast particles with a pulsed action was recently developed by using a gas heated by a shock wave (Refs. 40, 41). In this case, a gas jet discharged through an opening (Figure 6) in the end of a shock tube can be converted, after expansion, into a high-intensity molecular beam with effective velocities of the order of 1 to 10 ev (Ref. 40). The advantage of such a method is a relatively complete knowledge of the thermodynamic and physicochemical state of the gas, although it should be noted that certain deviations from these values, as will be shown below, are possible in the process of the shaping of the molecular beam. This source may be used as a convenient instrument for studying the kinetics of the chemical reactions developing in gases heated to high temperatures (Ref. 42). This method was used in Ref. 40, devoted to a study of molecular interaction in high-temperature gases by measuring the effective cross sections, and in Ref. 43, devoted to the measurement of the electron concentration behind a reflected shock wave. An obvious, although surmountable, difficulty of using such sources is the necessity of taking the measurements at the instant when the source is in operation, which is single-acting and of short duration (10 to 100 μ sec). This suggests that it is desirable to create a source with a periodic action. Such a source can obviously be based on the latest achievements in the technology of pulsed discharges in tubes (Ref. 44), using, for example, a pulsating impulsive discharge in which the charge-discharge of the battery and the injection of the working gas are synchronized. By removing the charged component from the jet, it is possible to obtain a beam of neutral particles with energies of several (up to 10) electron-volts. The use of an electrodeless discharge can substantially improve the homogeneity of the beam composition. No data have thus far appeared in the literature concerning the realization of such a project.

7. Recording and selection of molecular beams. The problem of detecting molecular beams is the second part of the dual problem of raising the level of the useful signal. Fast particles (with energies above 100 ev) are usually recorded by means of secondary electron emission; detectors for particles with gas kinetic velocities will be described below. The literature contains a large number of descriptions of various detectors, which may be subdivided into the following principal groups: /295

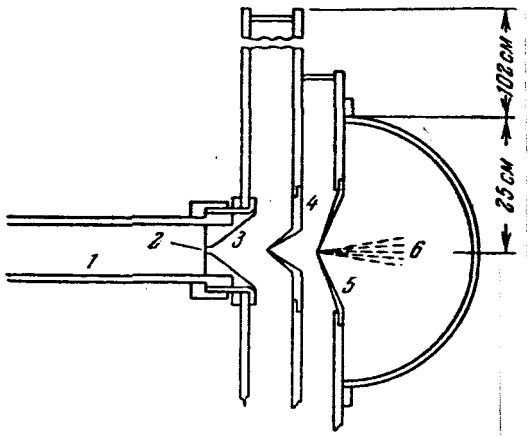

Figure 6. Schematic representation of a pulsed source of molecular beams, using a gas heated by a shock wave (Ref. 40)
1-Shock tube; 2-film diaphragm; 3-nozzle; 4, 5-shaping slits; 6-beam.

1. Universal detectors.

2. Detectors with surface ionization.

3. Manometric and Stern-Pirani detectors.

4. Sensitive balances.

5. Semiconductor and condensation detectors.

These types of detectors are discussed in detail in Ref. 1, and here we shall therefore dwell only on some new developments which appeared after its publication.

Universal detectors, which are the most promising, are based on the impact ionization of the beam particles by electrons and the collection of the ions formed for their subsequent recording. The higher the density of the electron current and the effective path traveled by the electron in the ionization space, the higher the efficiency of the ionization detector. These features are used as much as possible when ionization detectors are designed. To this end, the source of an electron beam is often built in the form of a Pierce gun (Refs. 45-48).

In order to increase the ionization efficiency, a magnetic field whose lines of force are parallel to the direction of motion of the electrons is used. This arrangement permits an increase of one order of

magnitude in the ion currents in certain designs (Ref. 49). A promising feature is the use of a hollow cathode as the ionizer, which provides an electron-current density exceeding the capacity of ordinary guns by one order of magnitude or more (Ref. 27).

Positive ions formed by the ionization may be used in two ways. First, they may be brought together on the ion collector connected by a load resistance to the input amplifier stage (Refs. 47, 50-52). The other possibility is to accelerate the ions extracted from the region of ionization to energies of ~10 kev, and to direct them into the first stage of a secondary electron multiplier (Refs. 46, 48-49). The use of an electron multiplier requires the preliminary separation of ions according to their masses, since the background formed by the residual gas would interfere with the recording of signals.

The sensitivity of universal detectors with multipliers is very high and makes it possible to record separate ions; for an ionization efficiency of 0.01, this means that it is possible to record beams of thermal velocities with a very low intensity, 10^4-10^6 molecules/sec. A detector of neutral beams with energies of 50 to 500 ev is described in Ref. 55.

When the ion current is amplified directly, the recording is substantially facilitated if the beam is modulated (Refs. 53, 54). An effective means of further amplification of the sensitivity is the use of synchronous detection. Such a recording arrangement is discussed in Ref. 47. Universal detectors are very convenient for relative measurements, but they must be calibrated for absolute measurements.

A very convenient and fairly simple device for absolute measurements is a capacity-type membrane manometer developed in Ref. 56 and having a sensitivity of $2 \cdot 10^{-6}$ mm Hg per scale division. The instrument is characterized by a great stability of the zero, simplicity of the readings, /296 and independence of the sensitivity from the absolute value of the pressure produced by the beam.

Condensation detectors have been used by a number of authors, but since a detailed analysis of this problem may be found in Ref. 57, we shall consider here only a recently proposed detector (Ref. 58), which simplifies and speeds up the measurements considerably. The sensing (receiving) element of this detector is a quartz crystal wafer maintained at a constant temperature which constitutes the resonance element of a generator with a frequency of 10 Mc. As the molecules of the beam are deposited, the mass of the crystal changes, causing a change (decrease) in the resonance frequency. This change in frequency can be measured very accurately. The sensitivity of the detector is so high that it permits the recording of changes in mass not exceeding 10^{-9} g. A similar device was developed by Akishin and Zazulin (Ref. 59).

Detectors based on the principle of a sensitive balance, and permitting the measurement of the transferred momentum under certain assumptions on the nature of particle reflection have found a widespread acceptance (Refs. 30, 32, 60-62). For absolute measurements, however, it is necessary to know exactly the intensity of the molecular beam. The use of such detectors has made it possible to evaluate the energies of particles knocked out by cathodic atomization (Refs. 30-32) through the measurement of the aerodynamic forces (Refs. 60, 61) acting in a stream of highly rarefied gas. The sensitivity of such devices attains 10^{-6} dyne for a precision of 0.2 percent (Ref. 62), although they are characterized by a long time lag.

In conclusion, we shall consider the original method (Ref. 63), which is the electron-optical analog of the shadow method known in optics. The method is based on the analogy between the refraction of a light beam and the scattering of an electron beam in gases, and the independence of the cross section from the pressure.

The principle of the method is apparent from Figure 7. The deflection of the electron beam scattered by the beam molecules causes it to bypass the "Foucault blade" placed at the focus of the electron-optical system in the absence of the beam. The requirement limiting the use of this system is the necessity of raising the density of the particles in the beam substantially above the density of the residual gases. If this is done, the synchronous modulation of the molecular and electron beams makes it possible to study the distribution of both the density of a bunch of particles and (using the change in density with time) the velocities of the particles of this bunch (Ref. 64).

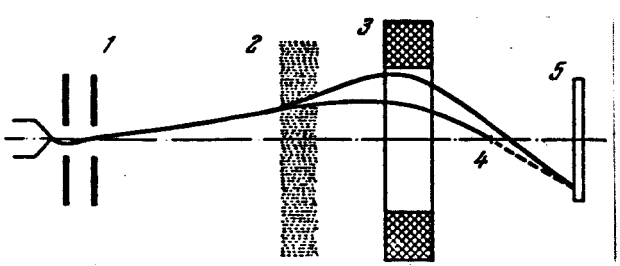

Figure 7. Diagram of the detection of molecular beams (Ref. 63)
1-Electron beam; 2-molecular beam; 3-electron-optical lens;
4-"Foucault blade"; 5-detector (photographic plate).

Finally, we shall briefly examine the methods of selecting a molecular beam, by which is meant a controlled regulation of the velocities of the beam particles. The use of a molecular beam with a Maxwellian velocity distribution renders the processing of the data difficult, and, /297

as will be evident further, obscures valuable details. For this reason, modern experimental devices usually include a molecular beam selector. The operational principle of a mechanical velocity selector is well known (Refs. 2, 65, 66), and the selectors which have been used recently are distinguished by a high accuracy and a low beam attenuation ("transparency"). An original design solution is the use, in Ref. 66, of two independent low-power motors (8000 rpm) for the rotation of the selector discs. The use of a synchronous motor enables us to change the angle of relative displacement of the slits on the discs with great accuracy (velocity straggling, less than 1 percent) virtually between any limits by a simple phase shift of the supply voltage. In the last few years, the so-called multiple-disc selectors have been widely used (Refs. 67-69). Ref. 67 describes a 6-disc selector providing a high accuracy (~5 percent) of selection at a high "transparency", achieved by bringing the number of slits on the disc up to 278; an 8-disc selector with 360 slits is described in Ref. 68.

An analytical treatment of the problem of calculation of a multiple-disc selector is given in Ref. 70. In this work, criteria for the selection of optimum parameters of the selector were found, and a bibliography of almost all the published works on mechanical selectors is given.

A simple method of measuring the velocities and isolating particles of a given velocity is the "time-of-flight" selection. The principle of this method is based on the spreading in space of a bunch of particles formed by the rotation of a disc with narrow slits. The difference in the particle velocities of the original pulse (of square-topped shape) causes it to blur during its flight to the detector. Having recorded the change in the ion current of the detector with time, we can immediately reconstitute the particle-velocity distribution curve, using the oscillogram. It can be readily shown (Ref. 71) that when the detection time τ (duration of the pulse) is small compared to the time of flight T over a distance L from the disc to the detector, the number of particles with velocity v ($v = L/T$) is related to the instantaneous value of the ion current i(T) as follows:

$$f(v) \sim i(T)T.$$

Figure 8 shows oscillograms of ion currents for beams of argon (1), hydrogen (5) and their mixtures (2-4) treated by this relation. The accuracy and simplicity of this method are desirable features which distinguish it from the method usually employed. When an electronic gating device is used, this method may make it possible to record particles of a given velocity selectively.

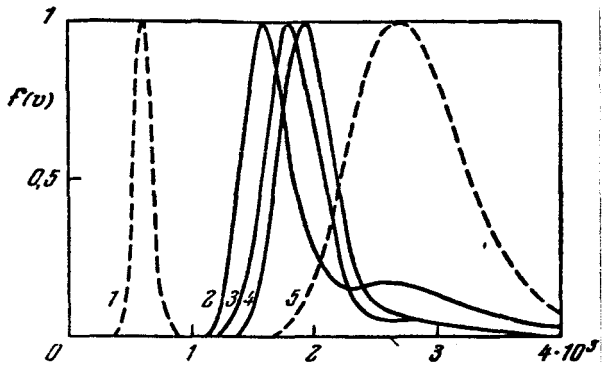

Figure 8. Processed oscillograms of the time-of-flight scanning of a modulated beam for various pressures of the initial mixture (2 percent Ar-98 percent H_2)

The ordinates of the curves correspond to the instantaneous values of the ion current. The time (and hence, the longitudinal) separation of the components of the mixture and the sharp increase in the relative content of Ar in the beam are clearly visible (Ref. 71).

3. APPLICATIONS OF THE MBM

/298

1. Elastic scattering of molecular beams and study of intermolecular forces. The study of elastic scattering in gases is one of the most fruitful applications of MBM and a direct source of information on the forces operating between atoms and molecules. As we know (Ref. 72), information of this kind may also be obtained in other ways, such as: direct quantum-mechanical calculation (which can be performed only for the simplest systems); study of the thermodynamic and kinetic properties of gases; measurement of the broadening of lines as a result of pressure in the microwave range; study of the thermodynamic properties of inert gases in the crystalline state, etc. The MBM supplements these methods in the range of energies corresponding to low and room temperatures. However, it is the only means with a sufficiently sound theoretical basis for the study of molecular interaction in the range of energies corresponding to temperatures above 1000°K. Furthermore, the MBM is practically the only method which permits a study of this interaction in the case of dissociated atoms.

At first, without entering into a detailed exposition of the theory of elastic scattering (Refs. 73-76), we shall write certain expressions which are necessary to illustrate the technique of determining a potential from data obtained by studying elastic scattering; then we shall

consider some specific examples. In the classical theory of scattering, a single-valued relation is established between the angle of deflection (χ) of the initial trajectory of the particle and the parameters of the force field of a stationary scattering center:

$$\chi = \pi - 2\theta_m = \pi - 2b \int_{r_{\min}}^{\infty} \frac{dr}{r^2 \sqrt{1 - \frac{V}{E} - \frac{b^2}{r^2}}}. \quad (1)$$

The symbols are evident from Figure 9; E is the initial kinetic energy of the particle, and V is the potential energy of interaction.

The differential scattering cross section, which determines the relative number of particles of the axisymmetric beam scattered at an angle between χ and $\chi + d\chi$ and equal to the number of particles traversing the target distance included between b and b + db is expressed as follows:

$$dQ(\chi, E) = \frac{1}{2\pi \sin \chi} b \left| \frac{db}{d\chi} \right|. \quad (2)$$

Using (1) and (2), one can show that for a potential of the simplest form, $V = K/r^s$ (we shall confine our treatment to this potential only),

$$dQ(\chi, E) = \left(\frac{K}{E}\right)^{2/s} \Phi(s, \chi), \quad (3)$$

where $\Phi(s, \chi)$ in the case of small-angle scattering has the form (Ref. 73) /299

$$\Phi(s, \chi) = \frac{1}{s} f(s)^{2/s} \chi^{-\frac{2s+2}{s}},$$

$$f(s) = \sqrt{\pi} \frac{\Gamma\left(s + \frac{1}{2}\right)}{\Gamma(s/2)}$$

(Γ is the gamma function). For the case of scattering at larger angles, numerical calculations of $\Phi(s, \chi)$ at $6 \leqslant s \leqslant 14$ were carried out in Ref. 77. In the case of potential functions of more complex type (with a minimum), numerical calculations are possible, and their results are given in Refs. 78-80).

The complete cross section characterizing scattering at angles from zero to π is given by:

$$Q(E)=2\pi\int_0^{\pi} dQ(\chi, E)\sin\chi\, d\chi. \qquad (4)$$

This expression diverges for any type of potential which does not become identically equal to zero at infinity. Therefore, the concept of an effective cross section of scattering at angles greater than some minimum angle which defines the resolving power of the apparatus is introduced in the classical theory of scattering. Then, with the approximation of small angles,

$$Q(E, \alpha)=2\pi\int_{\alpha}^{\pi} dQ(\chi, E)\sin\chi\, d\chi=\pi f(s)^{\frac{2}{s}}\left(\frac{K}{E}\right)^{\frac{2}{s}}\alpha^{-\frac{2}{s}}. \qquad (5)$$

What is a reasonable value for the minimum angle of deflection? The order of magnitude α may be determined, for example, from the condition of applicability of classical mechanics. Using the uncertainty relation, we can represent α in the form

$$\alpha > \frac{h}{2\pi\mu v\cdot 2b}=\theta^*, \qquad (6)$$

where μ is the reduced mass and v is the relative velocity.

For angles of deflection much greater than θ^*, the quantum effects may be neglected. Thus, $\alpha = k\theta^*$, where k is a numerical factor whose value should be determined.

In the quantum theory of scattering, the divergence of the total cross section is absent (at $s > 2$), and the corresponding expression is (Ref. 75)

$$Q_q(E)=\pi\frac{2s-3}{s-2}f(s)^{\frac{2}{s-1}}\left(\frac{4\pi K}{h\nu}\right)^{\frac{2}{s-1}}. \qquad (7)$$

If we substitute $\alpha = \theta^*$ into (5), we obtain an expression which at $s = 6$ differs from (7) only in the factor which is close to unity.

The experimentally effective scattering cross section is determined from the attenuation of the collimated monoenergetic beam which has passed through a homogeneous layer of the scattering gas,

$$Q(\alpha, E)=\frac{1}{nl}\ln\frac{I_0}{I}, \qquad (8)$$

where I and I_0 are the intensities of the scattered and nonscattered beam, respectively, n is the density of stationary scattering particles, /300

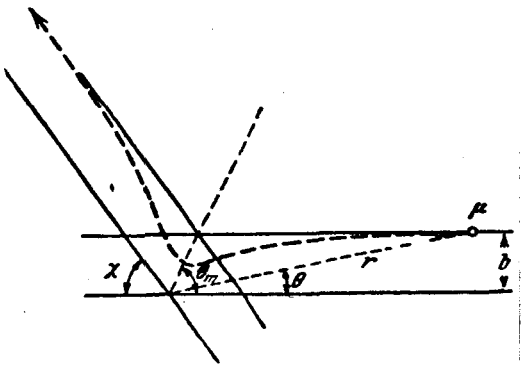

Figure 9. Schematic representation of the scattering of an atom by a center of force

and l is the length of the scattering path. In actual experiments, it is not always possible to attain the stationary or monoenergetic state of the interacting particles. It is therefore necessary to introduce corrections into expression (8) which allow for deviations from an ideal experiment. Calculations of the numerical values of such corrections, which are useful to experimenters, were made in Ref. 81. Since the measured value of the effective cross section Q (α, E) will depend on the resolving power of the apparatus, we are faced with the problem of an optimum choice of a resolving power which would insure an objective measurement of the total cross section.

We shall later return to the problem of selecting a resolving power, and will now indicate some methods of determining the potential parameters from the measured values of the cross sections. Using formulas (5), (7) and (8), we can write

$$\frac{1}{nl}\ln\frac{I_0}{I}=\pi\left(\frac{K}{E}\right)^{-\frac{2}{s}}f(s)^{\frac{2}{s}}\alpha^{-\frac{2}{s}}, \tag{9a}$$

$$\frac{1}{nl}\ln\frac{I_0}{I}=\pi\frac{2s-3}{s-2}f(s)^{\frac{2}{s-1}}\left(\frac{4\pi K}{hv}\right)^{\frac{2}{s-1}}, \tag{9b}$$

$$d\theta(\chi, E)=\frac{1}{s}\left(\frac{K}{E}\right)^{\frac{2}{s}}f(s)^{\frac{2}{s}}\chi^{-\frac{2s+2}{s}}. \tag{9c}$$

These relations, together with the differential cross section, are basic for finding the parameters, the quantum relations being usually employed for beams of thermal velocities, and the classical ones for fast velocities. From (9), where K and s are unknown, and the measurable quantities are Q (α, E) and dQ (χ, E), it is apparent that by varying n at constant E or E at constant n, it is possible, in the former case, to determine K when s is known, and in the latter case, to determine both K and s. It

is readily seen that the variation of n and E at a constant resolving power α can provide another convenient method of determining the parameters K and s.

In accordance with what was stated above, research involving the study of the elastic scattering of molecular beams may be arbitrarily divided into three groups: (1) finding the resolving power of the apparatus permitting an objective measurement of the total cross section, and finding the limits of the region of the deflections described by classical mechanics; (2) determination of the potential parameters and of the nature of the forces of interaction from measurements of the cross sections.

The problem of the resolving power was discussed in Refs. 82-84, and the related problem of the limit of applicability of the classical method was treated in Ref. 82. The essential point is that for a given resolving power of the apparatus, the experimenter should first be able to evaluate the extent of the deviation of the measured value from the total cross section, and second, to know whether the measured deviations fall into the quantum or the classical category. Such an analysis is justified by the illustration given in Figures 10 and 11. As is evident from Figure 10, the magnitude of the measured cross section may change substantially with a change in the resolving power. Furthermore, it is evident from Figure 11 that the classical description of the scattering in the range of small angles ceases to hold at a certain angle, beginning with which the experimental points fall satisfactorily on the curve calculated from the quantum formulas (Ref. 82). It is evident, therefore, that before trying to find the potential parameters, for example, we must determine both the resolving power and the range of angles investigated. /301

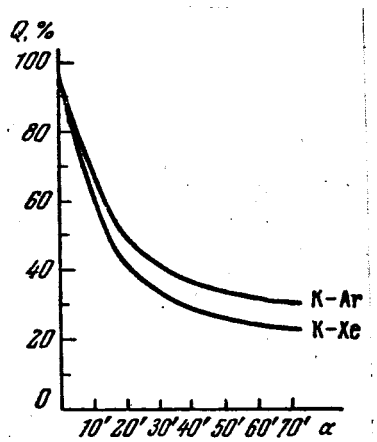

Figure 10. Measured effective scattering cross section versus resolving power of apparatus (Ref. 84)

An experimental transition from the classical to the quantum range of scattering (see Figure 11) was observed in a study of the angular distribution of scattered particles by means of an instrument of high resolution (several arc seconds in the laboratory system) (Refs. 81, 82, 84). For example, it was found that in the case of systems Na - Hg and K - Hg, k in the expression $\alpha = k\theta^*$ is equal to ~ 4 (this was also the case with other systems). This makes it possible to ascertain fairly accurately the limits of the classical description.

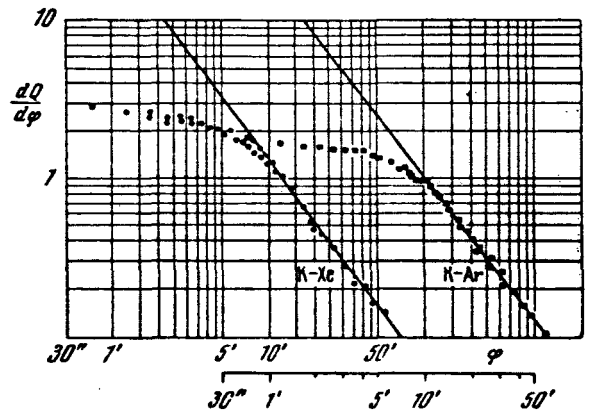

Figure 11. Differential scattering cross section versus angle of deflection (Ref. 84)
The straight line corresponding to formula (9) ceases to describe the experiment at angles of deflection of the order of 10' to 20'. The dependence in this region may be described by quantum relations by using the same potential parameters (Ref. 72); φ is the angle of deflection in the laboratory system.

The monograph of Massey and Barhope (Ref. 85) offers a method of evaluating the required resolving power, based on an approximation which assumes that the interacting particles are rigid spheres. According to Ref. 85, the error made in the determination of the cross section will not exceed 10 percent if the resolving power $\alpha = \theta_0$ ($\theta_0 = h/2\pi\mu va$, a being the sum of the gas-kinetic radii). It is obvious, however, that the gas-kinetic radius, which is determined by the momentum-transfer cross section, cannot satisfactorily describe small-angle scattering in the presence of forces of attraction. Another, more rational criterion, is proposed in Ref. 82: a is substituted by a doubled maximum impact parameter

$$\alpha = \theta^* \qquad \left(\theta^* = \frac{h}{2\mu v \cdot 2b}\right) .$$

As was to be expected, θ_0 and θ^* differ appreciably in magnitude; thus, for the system Na - Hg, $\theta^* = 2.3$ min, and $\theta_0 = 78.9$ min. An experimental study of the angular distribution of particles scattered at small angles has shown that particles scattered at angles less than θ^* no longer make any significant contribution to the value of the cross section (see Figure 11). Figure 12 shows the dependence, obtained in these experiments (Ref. 79), of the relative error made in the measurement of the total cross section on the magnitude of the resolving power, expressed in units of the critical angle θ^*. /302

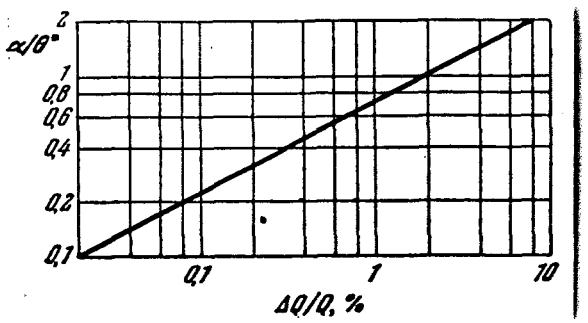

Figure 12. Relative measurement error versus resolving power, expressed in units of the critical angle (Ref. 82)

Comparing these data with those of Massey and Barhope, we observe a significant discrepancy (which is greater the more pronounced are the long-range forces of attraction).

The results examined above remove the doubts expressed in Ref. 83 concerning the possibility of an objective measurement of the total cross section, and lead to the conclusion that the data presented in Table II correspond very accurately to the total cross sections.

In work with fast particles (energies above 100 ev), the problem of resolving power becomes much less acute. This is because, as the velocity increases, the value of the limiting angle θ^* decreases, and the result may be that the resolution which would make it possible to measure the total cross section is practically unattainable. Therefore, use should be made in this case of the effective scattering cross sections described by formula (5), which will apply if the aperture angle is chosen large enough so that the quantum effects will not be able to manifest themselves. For instance, in the case of a beam with an energy of 1000 ev, quantum effects are possible at angles of 10" for Ar and 1.5' for He. If the resolving power of the instrument is known exactly, the potential parameters may be found by using (9a).

Table II. Total elastic scattering cross sections ($Å^2$) measured for beams of thermal velocities

Beam	Scattering gas								Reference
	H_2	D_2	He	Ne	Ar	N_2	O_2	Hg	
Li	120	124	106		301				88
			113		365				89
Na	154	182	132	211	403				88
						556		1995	82
					430	606	386		84
			247		480	689	510		107
K	176	227	167	261	580				88
	196	254	171		592	615			89
						680			82
						490			90
						470		2190	82
						755			91
								1820	13
Rb	173	211	154	266	572				88
						774		2552	92
Cs	176	216	163	289	572				88
					860				92
						908		3019	82
			470			926			93

We shall now consider some specific data (obtained in the last few years) on the scattering of both slow and fast beams, excluding inelastic collisions (Refs. 86, 87) from consideration. The principal results of measurements of the total cross sections of beams having thermal velocities are collected in Table II, from which it is evident that the agreement between the data of the different authors is quite satisfactory (account should be taken of the possible differences in beam velocities, of the dependence of the cross section on the velocity, and of the inaccuracy in the measurements of the density of the scattering gas). Moreover, a uniform treatment (carried out in Ref. 94) of the data obtained /303 from a measurement of the cross sections in the system K - Ar (Refs. 88-90, 92), using numerical results (Ref. 81), has shown that the deviations of the cross section values given by the various authors from the arithmetic mean do not exceed 2 percent. Such a good agreement makes it possible to adopt this value as a standard, and thereby to decrease the uncertainty in the measurement of the density of the scattering gas in

the subsequent experiments by taking control measurements of the gas. The only exceptions in Table II are the data of Ref. 93. The discrepancy is so large in this case that it caused Massey and Barhope to state in their monograph (Ref. 85) "As long as this problem remains unresolved, the results of the analysis of all the effective cross sections obtained from experiments with molecular beams must be carefully approached."

At the present time, this "compromising" discrepancy has apparently been successfully eliminated. Precision measurements of differential cross sections recently made with the aid of instruments with a resolution of the order of 3.5" in the range of angles up to 1° (a deflection of 16" was recorded as scattering) did not confirm the results of Ref. 93 for the system Cs - He; neither was an increase in cross section observed for the systems K - Ar, K - Xe, K - Br, and K - $HCBr_3$ (Ref. 84).

The experimental values of total cross sections can be used to find van der Waals constants if it is assumed that the interaction is due to dispersion forces (i.e., by setting s = 6). The values obtained in this manner can be compared with those calculated theoretically (Ref. 72). For the systems shown in Table II, the agreement is good. In Ref. 92, such a comparison was made for 100 different systems, and it was found that in 57 percent of the total number of systems the discrepancy between the theoretical and the experimental values was less than 1 to 3 percent, in 18 percent, from ±3 to ±6 percent, in 12 percent, from ±6 to ±10 percent, and in 13 percent, over ±10 percent. It was observed that the largest deviations corresponded to the scattering of particles of relatively low molecular weight.

A comparison of the measured cross section and van der Waals constants calculated from them with the theoretical values for the case of scattering of He, Ne, Ar, Kr, and Xe in argon was made in Ref. 95. The experimental values were observed to exceed the theoretical ones systematically, but the reason for this is unclear. An additional source of information on long-range forces of interaction may be the measurement of the dependence of the cross section on the relative velocity of the colliding particles. As follows from formula (7),

$$Q \sim v^{-\frac{2}{s-1}},$$

and if K is independent of v, then by varying the velocity we can obviously find the value of s (which is equal to 6 for a van der Waals interaction and is other than 6 for other types of interaction). In practice, a change in v is achieved by mechanical selection (Refs. 96, 99), or by the controlled change of the furnace temperature (Ref. 97). In Ref. 96, the dependence of Q on the velocity in the system K - N_2 was compared with the theoretical for s = 5, 6, and 7.

As is evident from Figure 13, the agreement between the theoretical and experimental values permits a single-valued selection of the value $s = 6$. A study of the velocity dependence of the total cross section for the scattering of a beam of the polar molecules of CsCl by polar and nonpolar gases is given in Ref. 97. In the case of scattering in a nonpolar gas, the results of the experiments are adequately described by the relation $Q \sim v^{-2/5}$ (if the theoretical values of K are used, the experimental points form a straight line of the type shown in Figure 13). However, in the scattering by a polar gas, the situation changes considerably. /304
The experimental dependence of Q on v (Figure 14) is characterized by an appreciable change in slope, and the numerical values of the cross sections change more in magnitude and their variation with temperature is greater. This effect may be accounted for if we take into consideration a dipole-dipole interaction in which, under certain conditions, the potential energy of the interaction may differ from that given by the effective spherically symmetrical potential (Ref. 72). These conditions are determined by the ratio of the period of rotation (τ_{rot}) to the interaction time (τ_{int}). When $\tau_{rot} \gg \tau_{int}$, the potential has the form

$$V = -\frac{\mu_1 \mu_2}{r^3} g$$

(where μ_1 and μ_2 are the dipole moments and g is a factor allowing for the orientation). This condition can be fulfilled by varying the temperature. In the work under consideration, however, the range of temperature change was insufficient, and the results permitted only a qualitative detection of the effect of interaction between two dipoles. A study of the interaction of polar molecules in the systems NH_3 and H_2O was made in Ref. 98.

Theoretical and experimental data indicate that the relation $Q \sim v^{-2/5}$ is poorly fulfilled in the case of interaction between light particles. A special experiment was carried out in Ref. 99 on the scattering of atomic and molecular hydrogen and helium in hydrogen and helium, which showed that the velocity dependence differs greatly from that predicted by the theory of Massey and Moore.

A deviation of the velocity dependence of the total cross section from the theoretical dependence was observed in Ref. 100 in a study of the scattering of a monoenergetic beam of Li by mercury. As the velocity of the Li atoms decreased, at some value of this velocity the magnitude of the cross section decreased sharply (this effect was absent in the case of K). Somewhat later, in a study of the scattering of an Li beam by inert gases (Ref. 101), deviations from the relation $Q \sim v^{-2/5}$ were also observed. The dependence on v in several systems (Li - Xe, Kr, Ar)

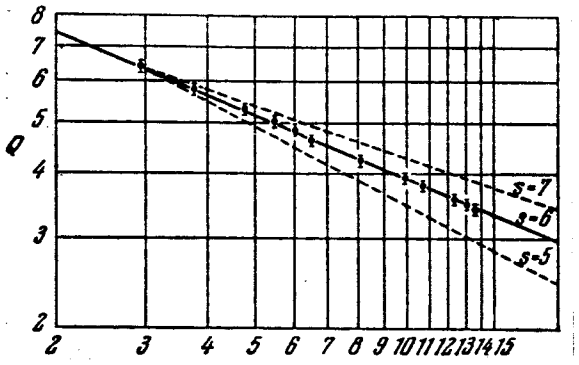

Figure 13. Effective cross section versus velocity of scattered particles
Straight lines correspond to formula (5) for s = 5, 6, and 7 (Ref. 96).

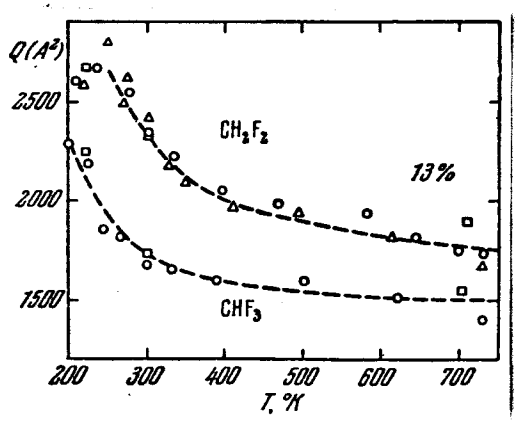

Figure 14. Effective scattering cross section of the polar molecule CsCl in polar gases versus velocity, expressed by the furnace temperature (Ref. 97).

was characterized by the appearance of relative maxima and minima. In Ref. 100, traces of quantum effects were also observed in small-angle scattering; in the range of angles up to 15°, the scattering curve shows fairly distinctly the periodicity predicted by the quantum-mechanical calculation.

Valuable information on the intermolecular forces may also be obtained by studying the angular distribution of particles scattered at large angles. In this case, measurements of the differential cross sections make it possible to restore the shape of the interaction potential, /305

i.e., to find the numerical values of the parameters for a selected functional shape of the potential. Monotonic potential functions of the form $V = K/r^s$ are the limiting possibilities of the description of the interaction for relatively large and relatively small impact parameters. The real interaction potentials, which describe interactions over the entire range of reasonable mutual distances, are not monotonic and possess a minimum.

These features of the potential function are reflected by the dependence of the deflection on the impact parameter during scattering, and cause the nonmonotonicity and multivaluedness of this dependence. The characteristics of scattering under these conditions were first generally treated by Firsov (Ref. 102), from whose work Figure 15 was borrowed. Figure 15a shows a typical nonmonotonic course of the dependence of χ on b^2 (deflections by repulsive forces were taken to be positive, and those by attractive forces, negative). Figure 15b shows the dependence of $db^2/d\chi$ on χ ($db^2 = 2dQ\ (\chi, E) \sin\chi\ d\chi$). Since in an actual experiment the positive and negative deflections are absolutely indistinguishable, the experimental dependence will obviously be given represented by a curve of the type shown in Figure 15c, which is the result of summing up the branches of Figure 15b. If the finite resolving power of the instrument is taken into account, the dependence of dQ on χ will be represented by the curve in Figure 15d. Figure 15d shows the fundamental characteristics associated with large-angle scattering, and discussed in later works (Refs. 78, 80). At the present time, following the publication of Ref. 80, the singularity corresponding to angle χ_0 is termed rainbow scattering (χ_0 is the rainbow angle whose magnitude for particles of fixed energy is uniquely related to the depth of the potential well; see Figure 15a); a series of characteristics of the scattering curve have been analyzed in Refs. 80, 104.

It should be noted that the above considerations apply rigorously to monoenergetic beams only; otherwise, these characteristics may be smeared and disappear altogether. This effect can be seen distinctly in Figure 16, which shows experimental data borrowed from Refs. 13, 103, 104. However, even in the case of nonmonoenergetic beams, the study of large-angle scattering makes it possible to find the values of the potential parameters. Thus, in Ref. 13, using the data obtained from a study of the scattering of K by Hg, $C_{16}H_{10}$, and $C_{14}H_{10}$ over a range of angles from 2 to 140°, the authors found the values of the parameters ε and r_m for Buckingham's "6-exp" potential.

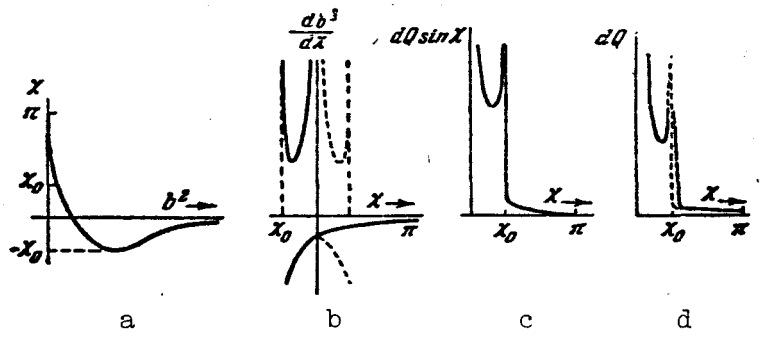

Figure 15. Qualitative representation of the scattering characteristics in the case of a nonmonotonic potential function of interaction (Ref. 102)

Based on the data on scattering in the region of the rainbow angle, /306 the r_m and ε parameters of Buckingham's α potential were found in Ref. 104 for the systems K - Kr and K - HBr (for the latter, in the region of elastic interaction). After careful examination, the author of Ref. 104 concluded that the treatment of the data on rainbow scattering requires the consideration of the quantum effects predicted in Ref. 80. The potential parameters may also be determined from the dependence of the differential scattering cross section on the relative kinetic energy, and such a study was made in Refs. 105, 106 for the systems Cs - Hg and K - Hg.

The above discussion shows that present-day advances in MBM engineering and progress in the analysis of scattering phenomena have given the experimenters effective means of studying intermolecular forces in the range of thermal energies.

In concluding the discussion of the scattering of beams of thermal velocities, it is necessary to indicate Ref. 107, a work unique in character which, in addition to being of interest from the physical point of view, is an illustration of the substantial progress made in experimental techniques.

It is well known that if only one of the partners is in the S state, the long-range forces are sensitive to the relative orientation of the interacting atoms. Thus, the goal set in Ref. 107 was to detect this orientation effect experimentally and to measure it quantitatively. The problem consisted, first, of obtaining monoenergetic beams of polarized atoms, i.e., beams with a given angle between the directions of the spin and velocity vector of the particles; and second, of detecting a difference in the measured values of the total cross sections which, on the basis of preliminary estimates, was no more than 1 percent of the value of the mean cross section.

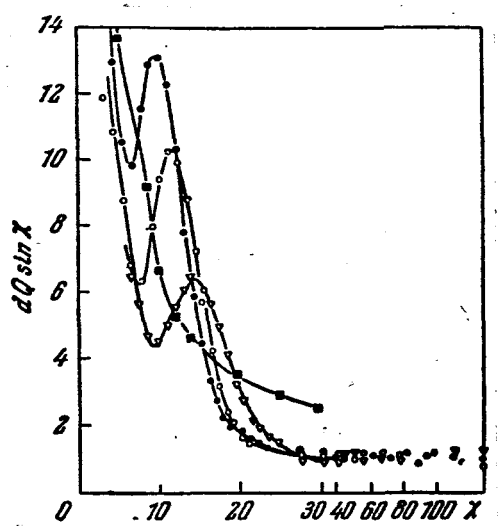

Figure 16. Experimental curves for the scattering of a monoenergetic (K - Kr - ▽, O, ●)(Ref. 104) and Maxwellian (K - Hg - ■)(Ref. 103) beam in the range of large angles; the effect of monokinetization is fully apparent. The curves ▽, O, ● correspond to different temperatures of the source of atoms.

In order to obtain polarized beams of Ga atoms, as in the Stern-Gerlach experiment, the effect of the spatial separation of the trajectories of polarized particles in an inhomogeneous magnetic field was used. Beams of differently polarized atoms were alternately emitted through the exit slit of this unusual source by changing the magnetic field intensity stepwise. Useful information on sources of polarized beams is given in Ref. 108.

After being monoenergized by the selector, the beam obtained passed through the scattering chamber, and the scattering cross section was measured in the standard manner by means of the attenuation of the beam intensity. In order to reduce the "depolarization" effects, the scattering chamber was placed in the field of a permanent magnet. In solving the second problem--the comparison of two cross sectional values differing by approximately 1 percent--an ingenious automatic scheme was used which made it possible to make such a comparison under conditions when, for an /307

accuracy of intensity measurements of 10^{-4}, the pulsations due to instabilities exceeded this value 100 or even 1000 times. The possibility of measurements under these conditions is due to a multiple recording of the attenuation of both beams at close time intervals and to the averaging of the results (by means of a storage device) for a long time interval in order to exclude fluctuations of random character. By use of a control

system which performed the automatic switching of the magnetic field and receiving channels, it was possible to record reliably and measure within 3 to 5 percent the difference in the scattering cross sections for beams of differently polarized particles. The technique employed by the authors in recording faint effects with a strong noise background may be regarded as a model in many respects, and certainly deserves serious consideration by the experimenters.

Let us now examine the principal results obtained by studying the elastic scattering of fast particles (with energies above 100 ev) and the possibility of practical application of these results.

The vigorous development of nuclear power and rocket engineering which has taken place in recent years has considerably sharpened interest in the study of the properties (particularly, kinetic properties) of high-temperature gases. For example, since a direct measurement of transport coefficients is impossible at the temperatures of interest, which range from one thousand to tens of thousands of degrees, the necessity of developing new methods by which the required data can be obtained is evident. The only quantity which characterizes a collision and which enters into the expression for the calculation of the transport coefficients is the angle of deflection of the particle trajectories. However, the study of elastic scattering makes it possible to measure these angles of deflection, or more properly, the probability of deflection at a given angle during the interaction with the corresponding energies. When these data are available and high-speed computers are employed, the problem of finding the transport coefficients becomes a comparatively simple one. Because of the relative simplicity of obtaining and recording particles with energies above 100 ev, the experiments involve the use of monoenergetic beams of particles of such energy, and the effects of grazing collisions at impact parameters of 1 to 3 Å are recorded, which corresponds to distances of maximum approach of particles at temperatures of the order of 1000 to 10,000°K.

A necessary condition for the interpretation of the results of the experiments is that the total elastic scattering cross section be substantially greater than the cross sections of the inelastic cross sections, a condition usually met in the selected energy range (100 to 3000 ev) (Ref. 85). As was indicated above, the description of the scattering of fast particles may be made rigorously within the framework of classical mechanics, and for this reason the K and s parameters of a spherically symmetrical potential of the type $V = K/r^s$ may be obtained by using expression (9a).

Table III gives practically all the experimental results obtained by measuring the dependence of the effective scattering cross section on

energy. It does not include the results of Ref. 124, which differ appreciably from those given in the table for the system Ar - Ar and Ne - Ne and obtained from measurements of the differential scattering cross sections. As is evident from Table III, data on the repulsion potentials of atomic-atomic, atomic-molecular, and intermolecular interactions have now been obtained.

The treatment of experimental data in the case of atomic-atomic systems is simple and was briefly described above. In the case where one or both partners in the collision are molecules, the treatment becomes more complex. Refs. 122, 123 propose a procedure for calculating the intermolecular potentials on the basis of data on the scattering of atoms (of /308
inert gases) by molecules. Since this method makes it possible to simplify considerably the manner in which data are obtained for intermolecular interaction at small distances, we shall examine it at some length. We shall use Figure 17, which is a schematic representation of the passage of a scattered particle past a molecule whose force field obviously is not spherically symmetrical. It is phenomenologically convenient to consider the problem of deflection of a particle by two spherically symmetrical centers; a certain effect of such scattering, averaged over the orientation (angles θ, θ_1, Figure 17), is recorded in the course of the

experiment. The aim of the theoretical examination is to develop a method for determining from the experimental data the effective interaction potential of a free atom and an atom belonging to a molecule; this potential can then be used to determine the intermolecular potential. /309
Further treatment requires the following reasonably justified assumptions: (a) during the interaction, the scattering molecule is considered to be a stationary, rigid body, so that no rotation or vibrations take place during that time; (b) the atoms forming the molecules are independent (additivity), spherically symmetrical point centers of force (with potentials

of the form $V = K/r^s$); (c) all the mutual orientations are equiprobable. As is evident from Figure 17a, the distance R between the scattered atom and the center of force

$$R = r(1 \pm 2\alpha\cos\theta + \alpha^2)^{1/2}, \quad \alpha = \frac{a}{r}.$$

Therefore, the total potential for a certain orientation θ is

$$V_{AM} = \frac{K}{r^s(1+2\alpha\cos\theta+\alpha^2)^{s/2}} + \frac{K}{r^s(1-2\alpha\cos\theta+\alpha^2)^{s/2}}.$$

Averaging over all the (equiprobable) orientations, we get

$$\overline{V}_{AM} = \frac{2K}{r^s}\frac{(1+\alpha)^{s-2}-(1-\alpha)^{s-2}}{2\alpha(s-2)(1-\alpha^2)^{s-2}}. \qquad (10)$$

Table III. Interaction potential of various systems in the range of repulsive forces

System	Potential $V(r)\cdot 10^{12}$, erg; r, Å	Distance range, Å	Reference
He—He	$0.201/r^{4.95}$	0,5—1	109
He—He	$4.62/r^{1.79}$ or $314\exp(-4.12r^{1/2})$	0.52—1.02	110
He—He	$7.55/r^{5.94}$	1.27—1.59	111
He—He	$5.56/r^{5.03}$	0,97—1,48	112
Ne—Ne	$500/r^{9.99}$	1,76—2.13	113
Ar—Ar	$46.1/r^{4.33}$ or $3.66\cdot 10^4\exp(-6.82r^{1/2})$	1.37—1.84	114
Ar—Ar	$1360/r^{8.33}$	2,18—2.69	115
Kr—Kr	$255/r^{5.42}$	2,42—3,14	116
Xe—Xe	$1.1310/r^{7.97}$	3,01—3,60	117
He—Ar	$99.5/r^{7.25}$	1,64—2.27	118
Ne—Ar	$1010/r^{9.18}$	1,91—2,44	119
H—He	$3.75/r^{3.29}$	1,16—1,71	120
H—H_2	$70.8\exp(-2.99r^2)+6.07\exp(-0.942r^2)$	0.27—0,68	121
D—D_2	$45.9\exp(-5.17r^2)$	0,29—0,56	121
He—N_2	$119/r^{7.06}$	1.79—2.29	122
Ar—N_2	$1210/r^{7.78}$	2,28—2,83	122
N_2—N_2	$954/r^{7.27}$	2,43—3,07	122
He—CH_4	$965/r^{9.43}$	1,92—2,37	123
He—CF_4	$9.9\cdot 10^6/r^{17.51}$	2.43—2,74	123
CH_4—CH_4	$9.63\cdot 10^6/r^{15.47}$	2,47—3,06	123
CF_4—CF_4	$1.87\cdot 10^{22}/r^{39.27}$	3,43—3,77	123

From the structure of this expression, it is apparent that the mean total potential is equal to twice the interatomic potential, with a correction allowing for nonsphericity. The second factor approaches unity as r increases. In principle, the expression obtained should now be substituted into (1), and a functional relation between the cross section, the potential parameters and the energy should be found. Then the experimental dependence of the cross section on the energy could be used to reconstitute the type of the potential, i.e., to find the K and s parameters. However, it will not be possible to obtain an analytical expression of the type of (5) in this case, and Ref. 122 suggests another method. Let us note that the use of machine calculation may solve this difficulty, but the method discussed above is not sufficiently clear physically.

Let us thus assume, as in Ref. 122, that within the experimental errors the scattering of atoms by molecules is described by some spherically symmetrical effective potential $V' = K'/r^{s'}$. The numerical values of K' and s' can then be readily obtained from the experimental dependence of Q (α) on E. Further, it is of course possible to select values of K and s for which formula (10) will describe the course of V' (r) with

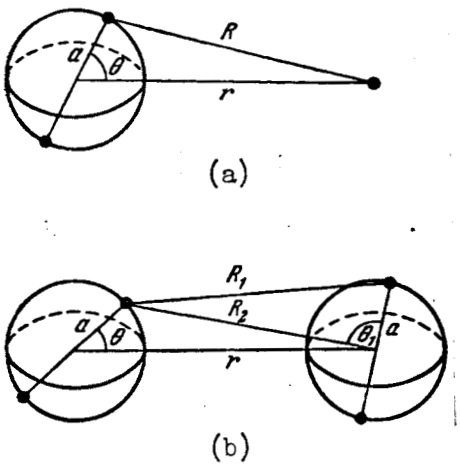

Figure 17. Configuration of particles used in calculating atomic-molecular and intermolecular repulsion potentials

sufficient accuracy over a given energy range. This in brief is the method of determining the parameters of the effective interatomic potential. These parameters are obtained for systems of unlike atoms (He - $(N)_2$, Ar - $(N)_2$, etc.). To find the effective interatomic potentials for homonuclear molecules, we will use the empirical combination rule, which has been experimentally verified on atomic systems. The combination rule (Ref. 72) permits us to find the potential parameters of the interaction of like atoms (K_{ii}, s_{ii}) from their values for unlike atoms (K_{ij}, s_{ij}), and has the form

$$K_{ij}=\sqrt{K_{ii}K_{jj}},\quad s_{ij}=\frac{1}{2}(s_{ii}+s_{jj}).$$

This is precisely the way in which the parameters of the effective interatomic potential of interaction of like atoms are obtained from the values obtained. The intermolecular interaction potentials are determined from the obtained effective interatomic potentials in the following manner. As follows from Figure 17b, /310

$$R_1=r(1\pm 2a\cos\theta+a^2)^{1/2},$$
$$R_2=(R_1^2\pm 2a\cos\theta_1+a^2)^{1/2}.$$

Here, in contrast to the atomic-molecular systems, another angle (θ_1) is introduced, which characterizes the mutual orientation. Knowing the effective interatomic potential and using the assumption on additivity, we

can write the total potential of interaction of four atoms, and, after averaging over the angles θ and θ_1, obtain

$$\overline{V}_{MM}=\frac{4K}{r^s}\frac{(1+2a)^{s-3}-(1-2a)^{s-3}-2(1-4a^2)^{s-3}}{4a^2(s-2)(s-3)(1-4a^2)^{s-3}}.$$

Having constructed the dependence of $\overline{V}_{MM}$ on r with the aid of the known parameters of effective interatomic interaction, K and s, we can select values of K* and s* such that this dependence be described with sufficient accuracy over the given energy range by a potential of the form $V^* = K^*/r^{s^*}$. These are the parameters K* and s* shown in Table III for the systems N_2 - N_2, CH_4 - CH_4, and CF_4 - CF_4.

The effectiveness of the method of fast-particle scattering as a means of studying repulsive forces cannot be overemphasized. However, the presence of the material presented in Table III appears to indicate that the possibilities offered have not yet been fully exploited. It seems desirable at this point to discuss briefly the possible inaccuracies of the cited results.

A check of the results could be a comparison with the analogous results of other authors. Unfortunately, this is still impossible. As was mentioned above, the old results obtained in Ref. 124 differ considerably from those given in the table. An indirect checking method is the "matching" of potential curves extrapolated to great distances with those obtained from measurements at normal temperatures. According to Ref. 125, however, this method cannot be considered unambiguous and sufficiently justified. Still another method of checking consists in a comparison with the theoretical trend of potential curves calculated for the simplest systems; in this case (Ref. 126), the experimental values are observed to be considerably too low as compared with the theoretical ones for small distances.

The main sources of possible experimental errors in these measurements should be indicated. One of them is an insufficient determinacy of the resolving power of the apparatus.

An inadequate localization of the scattering region was responsible for the fact that in these experiments the geometrical aperture was not equivalent to the resolving power, and the effective resolving power was determined by a complex calculation which required the use of the determinable parameters K and s (Ref. 110). A recent series of works (Ref. 109) devoted to a redetermination of the potential parameters deals with attempts to overcome this defect.

It is evident that this defect is the main factor responsible for the difference in the results obtained for a narrow and a broad detector.

Another source of error in these experiments (which is also inherent in other scattering work as well) is the indeterminacy of the density of the scattering particles in the scattering chamber. There is also a certain indeterminacy in the beam composition, and a number of other, less important shortcomings. All this leads to the conclusion that the results obtained are only approximate, but this of course does not reduce their value.

Allowance for these defects and improvements in experimental techniques will make it possible to refine the existing results and to obtain very interesting new data, particularly on the interaction of dissociated, electron-excited atoms with atoms and molecules.

2. Use of the MBM in solving certain chemical problems. We shall /311 consider a set of works devoted to the study of chemical or phase transformations by means of the MBM processes. In these experiments, the MBM may be used, first, for a practically inertialess taking of the sample, which is then analyzed by some method, and second, for the study of the effects of inelastic interaction between chemically active atoms and molecules.

As was already indicated, the main feature of a molecular beam is the absence of interaction between its particles, and therefore the beam extracted from the source carries information on the thermodynamic and physicochemical state of the substance in the source. If, in addition, the escape of particles from the source does not disturb the state of the latter (as is practically always the case), it is evident that such a probe will be a very effective means of studying, for example, the relative composition, the energy distribution of particles in chemically inert and active mixtures, etc. The problem of distortion of the beam composition as compared to the source composition has been thoroughly treated in several studies (Ref. 127).

An analysis of the first works involving the MBM can be found in Ref. 128; the possibilities offered by such investigations have grown considerably in the last few years, and we shall specifically consider the most interesting results.

Data on the molecular composition of vapors over the surface of pure solid and liquid substances and compounds are of great interest in studying the properties of the condensed phase. We can study both the vapor at equilibrium and the composition of the vapor during evaporation from an open surface (Ref. 129).

In many cases, a mass-spectral analysis of the composition does not permit a definite conclusion to be drawn with respect to the vapor composition, i.e., the partial pressures of the various components at

equilibrium with the condensed phase. The values of the heat of vaporization also remain undetermined. Use of the MBM by means of an analysis based on precise measurements of the molecular velocity distribution in the beam formed by effusion from a furnace of known temperature (Refs. 130-132) successfully overcomes these difficulties. Moreover, since the experimentally obtained distribution is a superposition of the partial distributions, the composition can be determined by matching so as to make the theoretically calculated distribution coincide with the experimental one. In addition to determining the molecular composition, it is possible in these experiments to measure the vaporization coefficients, and the dissociation energy of polymeric formations in vapors (e.g., of alkali metals) (Ref. 130). Similar measurements, although less successful, were made in Ref. 131. At the present time, this method of analysis is being widely employed (Refs. 129, 132).

A promising possibility is the use of the molecular beam as a pulsed probe in the study of the kinetics of high-temperature physicochemical transformations. In this case, by extracting the beam from the region where the gas is strongly heated (up to several thousand degrees) and analyzing the beam composition, it is possible to study directly both the equilibrium composition and the kinetics of the reactions taking place (Ref. 42).

We have already examined the design features of pulsed sources based on shock tubes; in combination with a time-of-flight mass analyzer (with a time resolution of 10 to 100 μsec), such a device enables us to follow the chronological course of the reactions which occur. The value and potentials of this technique cannot be overemphasized. When it was employed in investigations of the thermal decomposition of N_2O, and the polymerization and oxidation of acetylene, it was possible to identify the intermediate products of the reaction and to measure the rates of individual reaction steps at high temperatures (Ref. 41). /312

A similar technique was used to study the thermal ionization behind the front of a shock wave (Ref. 43). The degree of ionization could be determined from the current of the charged component extracted from the beam.

Knowing the composition of a high-temperature gas or plasma and using the MBM, we can study the energy distribution of particles and thus estimate the temperature of the gas being investigated (Refs. 21, 133). A method for such an analysis of fast streams of neutral atoms coming from the discharge region was developed and successfully applied in Ref. 134. Such a method would apparently be useful in studies employing shock tubes.

One of the most promising applications of molecular beams is the study of the mechanism of homogeneous chemical reactions occurring during

the collision of particles of intersecting beams. Extensive experimental and theoretical work is being conducted in this direction at the present time, and we shall examine certain interesting results.

The use of molecular beams in the study of the mechanism of chemical reactions involves a difficulty due to the fact that the activation energy of most reactions usually exceeds substantially the average kinetic energies of beams of thermal velocities. Therefore, in setting up the experiment, we must select reactions with low activation energies, or raise the relative kinetic energies of the interacting particles in some way. Thus far, the main subjects of study have been alkali and halogen atoms and their compounds, for which it is possible to overcome the activation barrier and to develop simple detectors of adequate sensitivity.

The first work devoted to the study of chemical interaction in intersecting beams appears to be Ref. 135. One of its principal results was the development of a selective detector with surface ionization; this made it possible to record elastically and inelastically scattered particles separately. The activation energy of the studied reaction, $K + HBr \rightarrow KBr + H$ was calculated from the yield of the products at various temperatures of the source of K atoms, and was found to be 3.4 ± 0.12 kcal/mole. The value of the steric factor was also found. A comparison of the measured angular distributions of the products with those calculated by making various assumptions concerning the reaction mechanism (complex formation) and the magnitude of the activation energy permits certain conclusions with regard to the correctness of these assumptions. This possibility has an important fundamental significance and is a stimulus for the elaboration of further experiments.

An attempt to determine directly the activation energy of the same reaction was made in Ref. 136 by using a monoenergetic beam of K. The yield of the products observed at an angle of 35° in the laboratory coordinate system, starting from a relative energy of 1.4 kcal/mole, rose sharply with an increase in the initial relative kinetic energy of the colliding particles, reached a maximum at 3.3 kcal/mole, then dropped off gradually. This result, incomprehensible at first glance, was successfully explained by the influence of the kinematics of a collision (Ref. 137). In analyzing experiments of this kind, it is necessary to consider the dependence of the reaction probability, which is expressed by the differential cross section of the reaction, on both the vectors of the initial and final relative velocity and the angle between them. Therefore, in recording the effect of the reaction at a fixed angle in the laboratory system, when the absolute value of the initial velocity changes, it is necessary to take into account the change in the direction of the vector of the initial relative velocity. If this effect is neglected, the observed dependence on the velocity may be fictitious. /313

The calculations made in Ref. 137 have made it possible to interpret the data of Ref. 136 by taking the kinematic effects into account. Kinematically, the most convenient systems are K-CH_3-I and K-CH_5I, for which, in addition to the reaction cross section, it was possible to establish that the distribution of the vectors of the final relative velocity is characterized by a pronounced anisotropy (a predominant forward divergence of the products in the center-of-mass system), and that over 80 percent of the reaction energy (equal to 25 kcal/mole) is expended on the rotational and vibrational excitation of the molecules of the products. The reaction yield (total number of KI molecules divided by the total number of scattered K atoms) is of the order of 10^{-4}, which corresponds to a cross section of approximately 10 Å^2. The activation energy was found to be negligibly small--less than 0.3 kcal/mole (Ref. 138). A similar result was obtained for the system Rb-CH_3I (Ref. 139).

A study of the chemical interaction of a monoenergetic beam of K atoms with a beam of HBr was recently made in Ref. 140. Measurements of the reaction cross sections at various velocities of the K beam gave 0.4 kcal/mole for the energy threshold of the reaction, and showed a weak dependence of this cross section on the velocity up to relative energies of the order of 4.5 kcal/mole. The probability of the reaction was estimated in conjunction with the impact parameter b, and it was found that for b values smaller than 3.5 Å, 90 percent of the collisions result in a reaction. The estimated cross section of the reaction beyond the threshold is 34 Å^2. The difference between the measured activation energy and the value given in Ref. 136 is explained by the authors as being due to an improved method of measuring[1] the relative collision energies. It can be shown that this activation energy is very close in magnitude to the value measured for the systems K-CH_3I, and K-C_2H_5I (Ref. 138). The possibility of a chemical interaction in the system K-Cl_2 was noted in Ref. 141. In Ref. 13, the interaction of the atoms of the K beam in intersections with beams of $HgCl_2$, HgBr, HgI_2 and SnI_4 was observed, but the reaction cross sections could not be determined.

The principal information obtained in experiments with intersecting beams consists of the angular distribution of elastically and inelastically scattered particles, and the dependence of the yield (total and "differential") of the reaction products on the velocity of the colliding partners. We may be able to use these data to calculate the details

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[1]Tr. note: The word is "changing" in the original Russian.

of the reaction mechanism if, on the basis of a specific model, we can calculate theoretically the angular dependence of the products and select the parameters dependent on the model so as to obtain the necessary agreement with the experimental curve.

Such calculations, based on the law of conservation of momentum and energy, were carried out for the reaction K + HBr → KBr + H in crossed beams, with various assumptions concerning the dependence of the reaction cross section on the relative collision energy (Ref. 142). The use of monoenergetic beams and of heavy particles in the perpendicular beam simplifies the treatment considerably, but in this case as well there remains a difficulty due to a certain indeterminacy of the impact parameters of the collision and internal excitation of the reaction products. The complexity of the interpretation of the experimental data obviously does not diminish the value of this method in the study of elementary chemical reactions.

A recently proposed modification (Ref. 143) of the method of intersecting beams deserves some attention. In this case, a beam of chemically activated particles is passed through a chamber filled with a gas capable of reacting. As a result of the "evacuating effect" of the molecular beam, manifested in the expulsion of the gas molecules from the chamber, the reaction products enter the ionizer of the mass spectrograph. This method was used (Ref. 143) to carry out a preliminary /314
study of the reaction of electron-excited oxygen atoms (beam) with nitrogen dioxide (target). The source of the atomic oxygen was a tube in which a high-frequency electrodeless discharge took place.

The above method is very promising, but in order to obtain reliable quantitative data, it requires further improvement and the elimination of indeterminacies which it still contains.

The possibilities of experiments with intersecting beams carried out thus far have been seriously limited by the detection method used (surface ionization). The use of sensitive universal detectors in combination with mass analyzers will substantially expand the range of the divergence angles where the products can be observed, since the background of elastically scattered particles will not be affected. Of great promise is the ionization detector of a molecular beam, described in Ref. 144, in combination with a quadrupole mass analyzer. The high sensitivity and small size make it very convenient in such experiments.

The use of the above-described methods in modulation and time-of-flight selection may prove to be effective. In the time-of-flight selection, the time resolution of the ion current of the products with a synchronous recording of elastically scattered particles will permit the determination of the velocity of the reaction products. Thus, one more quantity will become known in the energy balance, and this will naturally facilitate the treatment and interpretation of the data.

Considering the progress already made in the techniques of obtaining and detecting beams, we can assume that the immediate future will bring a considerable expansion of research in this area. In conclusion, we should mention the extensive and still unused possibilities of studying the reactions of photoexcited atoms. The realization of these experiments will become possible with the recently developed powerful pulsed light sources.

3. Use of molecular beams in the study of phenomena accompanying escape into a vacuum. The development of the above-described gas-dynamical source has made it possible to study experimentally the gas-dynamical and physical processes accompanying the sudden expansion of a gas in a vacuum.

Thus, in Ref. 21, a molecular beam produced by a gas-dynamical source was used to study the deactivation of the internal (vibrational and rotational) degrees of freedom of molecules upon the expansion of the jet in a vacuum.

The first experiments of this kind were carried out in 1950 (Ref. 145), but in Ref. 21 the effect was recorded more directly by comparing the measured velocities of the beam particles with the velocities calculated with the assumption of a total or partial deactivation. It was found that at small dynamic pressures, the deactivation is not complete for heavy gas molecules (UF_6), in contrast to CO_2.

It is a well-known fact that there is a certain difference between the composition of the gas in the beam and the composition in the effusion source; this is due to the dependence of the probability of flight beyond the slit on the absolute value of the thermal velocity of the particle. Becker (Ref. 146) observed a sharp increase, incomprehensible at first glance, in the intensity of the obtained beam when mixtures of gases were blown through the nozzle. This increase is quite apparent in Figure 18a, where the ordinate axis gives the ratio of the intensities /315
of the beams formed at the same pressure from a mixture of gases and a pure component, respectively. This effect, essentially equivalent to the increase in the discharge of mass through the collimating slit, may be explained by the separation of the gas components in the supersonic jet and the increase of the relative content of the additive component, or, in other words, by saying that as a result of spatial separation due mainly to the difference in thermal velocities, the nucleus of the supersonic stream (from which the molecular beam is shaped) becomes rich in the heavy component, and its peripheral part, in the light component of the mixture.

According to Ref. 147, the possibility of separating gas mixtures in supersonic streams was first pointed out by Dirac, whose idea was

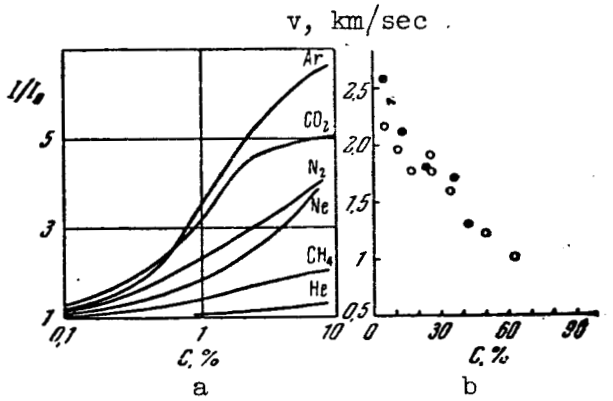

Figure 18. Increase in intensity associated with the use of a mixture of hydrogen with other gases in the gas-dynamical source (Ref. 146) (a), and dependence of the most probable velocity of the beam molecules on the initial concentration of N_2-H_2 mixture at two pressures (b) (Ref. 133)

essentially that the separating action of the gas centrifuge could be achieved without any moving parts in a jet whose lines of flow were curved. The forces which thus arise would act on the spatial distribution of particles of unlike masses in the same manner as in a centrifuge.

The separation phenomenon was studied in great detail in Refs. 146, 148, 149 in connection with an attempt to develop an industrial unit for the concentration of uranium. We shall briefly mention here the results which are of physical interest, and omit the technical aspects of these investigations.

The study of the separation effect made it possible to ascertain the influence of the geometrical factors on the efficiency of the separation, and this made it possible to localize the region of maximum separation to a certain extent. In Ref. 147, the authors, whose aim was similar, were able to establish the possibility of a "reversal" of the effect, i.e., a reduction in separation with increasing dynamic pressure; they also discovered the possibility of separating mixtures of particles of the same mass but different gas-kinetic cross sections--an effect which they termed "dimensional" diffusion. In order to increase the efficiency of the separating device, a study was made of the phenomena in additionally curved jets (Ref. 149). In addition to the enrichment of the nucleus with the heavy component, the phenomenon of separation is accompanied by another interesting effect--the acceleration of the heavy component (Ref. 150). Figure 8 shows oscillograms (normalized to unity) obtained by the above-described time-of-flight method for a beam consisting of the mixture

Ar (2 percent) - H_2 (98 percent) at various pressures. The dotted line shows the oscillograms --velocity distribution curves for pure Ar and H_2.

It is evident from Figure 8 that the faint maximum in the case of a mixture corresponds to the most probable velocity for hydrogen, and the second maximum to some velocity which considerably exceeds the most probable velocity for Ar. Obviously, this maximum can be explained only by the appearance of fast Ar atoms (accelerated in some way) in the beam. It is interesting to note that despite the small content of Ar in the initial mixture, the major part of the time-resolved pulse of ion current (see Figure 8) corresponds to argon particles. A similar result was obtained by the author of Ref. 133; Figure 18b shows the dependence of the most probable velocity in the beam on the initial concentration of the N_2-H_2 mixture. It is obvious that the acceleration of the heavy component produces the above-mentioned increase of its discharge through the collimating slit. The acceleration may be qualitatively explained by the fact that the particles of the heavy component are "carried along" by the jet at the average velocity of the mass motion. /316

The effect of separation and of the associated acceleration of the heavy component makes it possible to expand the possibilities of a gas-dynamical molecular beam source considerably. Thus, by using these effects, the author was able to obtain fast (up to 2 km/sec) beams of Ar, CO, N_2, O_2, etc., whose intensity was approximately three orders of magnitude greater than that of an effusion source under similar conditions. It is pertinent to note that a velocity of about 2 km/sec corresponds, in the case of Ar, for example, to the mean velocity at a temperature of the order of 10^4°K, i.e., to an energy of the order of 1 ev. The use of mixture preheating to temperatures of the order of 2000°K may produce intense beams with energies of 3 to 5 ev; the use of a high-frequency electrodeless discharge is promising. The acceleration effect may be used successfully in studying chemical reactions, since the acceleration may produce the energy necessary for overcoming the activation barrier.

Of undeniable interest is the possibility of using the MBM for investigating the condensation process (Refs. 22, 23, 146). In this case, the precooled gas (by liquid helium or nitrogen) is subjected to expansion in the nozzle, which is the first step of a gas-dynamical source. The composition of the shaped beam was analyzed for its mass, and the presence of "aggregates" composed of 2 to 7 molecules, along with individual molecules, was established in the mass spectrum (Ref. 151). Prior to the performance of the mass analysis, this "agglomeration" effect was evaluated on the basis of the sharp increase in beam intensity and changes in the velocity distribution (Refs. 22, 146). The measured current density

for the beam of cooled hydrogen exceeded 10^{19} molecules/cm^2 sec, which is two orders of magnitude greater than the maximum intensity for the case of discharge at room temperatures.

A beam of condensable particles is characterized by a slight expansion; this is of great interest from the technical standpoint, since it makes it possible to retain a high current density at large distances from the source. When mixtures of condensable and noncondensable gases (e.g., N_2 and H_2) were used, a considerable increase in beam intensity was observed, as could have been expected. Thus, for the mixture 20 percent N_2 - 80 percent H_2, the intensity increased 30-fold compared to the case of pure nitrogen at the same pressure. The enrichment of the beam with heavy condensable particles was responsible for the fact that, in an initial mixture of 25 percent H_2 - 75 percent He, the beam was found to contain 98.4 percent hydrogen.

The possibility of obtaining intense beams containing such "aggregates" provides the experimenters working in the field of the liquid state with a very interesting physical subject of study. Of major interest is the study of the structure and bond energy of these formations. Such beams also have a certain value as dense gaseous targets and in connection with the problem of injection of fast particles into magnetic traps, or, as was shown in Ref. 151, such complexes of particles may be ionized and accelerated.

4. Study of the interaction between molecules and the surface of a solid. The study of the problem involving the interaction with a surface /317 has been studied for a long time by various methods. An ideal experimental setup may be considered to be one in which a direct detection is made of the interaction of monoenergetic particles with a surface whose state is closely controlled. The MBM permits the closest possible approximation of these conditions.

The use of the MBM produces, in this case, an important improvement in experimental conditions--a factor which is sometimes fundamental in this problem--and permits a simplification of the treatment of the results obtained. The use of molecular beams in these problems is very effective from the standpoint of recording, since practically all of the beam particles take part in the interaction, so that the useful signal itself turns out to be stronger. The study of the phenomenon of diffraction of molecular beams on crystalline surfaces has already clearly demonstrated the great potential of the MBM.

As in the past, considerable attention is focused at the present time on the investigation of the interaction of beams of metal atoms with

a cold surface. Successful determinations have been made of the influence of impurities and surface purity on the efficiency of the condensation of the beam particles, on the regularity of migration of the atoms in the deposit, and on the structure of the deposit. A detailed analysis of the available material may be found in Refs. 57, 152-155.

When a body moves in the upper layers of the atmosphere, its surface is subjected to the intense action of an oncoming molecular flux. This action causes the deceleration and heating of flying devices.

The phenomena which are of interest in this connection and can be successfully studied by means of the MBM include, in particular: (1) reflection, scattering and adsorption of incident particles, (2) energy exchange between the stream of incident particles and the surface of the body, (3) deactivation of activated particles upon collision, surface recombination of atoms into molecules, of ionized particles into neutral ones, and the nature of the redistribution of the energy involved, and (4) the reverse problem of exciting internal degrees of freedom during a collision, surface dissociation and ionization.

The first studies on the reflection of molecular beams from surfaces are the previously mentioned works by Stern. Subsequently, a number of investigations were carried out which showed the possibility of a specular (diffraction) reflection from the surface of a spall of LiF crystal only for a very small number of gases (extremely light ones). Rising interest in this phenomenon, caused by the success of high-altitude flights, has led in the last few years to a renewal of intensive research on this problem. Reflection is quantitatively described by means of two quantities--the diffusivity coefficients (f) and specularity coefficients (1-f)--in accordance with the quantitative concept of the possibility of dividing particles into those reflected diffusely and those reflected specularly (without loss of velocity). By using these coefficients (and also the accommodation coefficient α), it is possible to find the aerodynamic characteristics of bodies of practically any shape, and thus to arrive at the optimum choice of shape.

However, there is no doubt that the simple qualitative model of interaction of molecules with surfaces, which first appeared as a working hypothesis, needs to be verified and confirmed. To this end, the investigation of the reflection of He and Ar beams from the surface of a spall of a LiF crystal was repeated (Ref. 154). The results obtained for He are in complete accord with those of Stern, and some additional new details were discovered. However, in the case of Ar, it was established that no traces of diffraction whatever were present, and that it was impossible to construct a scattering diagram by superimposing the streams of diffusely and specularly reflected particles. Thus, these results do /318 not confirm the hypothesis of a diffuse-specular reflection.

Refs. 62, 155-157 are also devoted to a verification of this hypothesis; in particular, the numerical values of the momentum transfer coefficients, which are more adequate macroscopic interaction characteristics, were determined. These coefficients are determined as follows:

$$\sigma_{n,t} = \frac{\pi_p - \pi_{neg}}{\pi_p - \pi_{st}}$$

where π_p and π_{neg} is the momentum, tangential (t) or normal (n), introduced by the incident molecules and carried away by the reflected ones. An experimental measurement of the angular distribution of the beam molecules reflected from the surface makes it possible to find the numerical values of σ_n and σ_t. The results obtained point to the possibility of deviation of σ_n and σ_t from the values corresponding to the idealized case, and to the indeterminacy of dividing the particles into diffusely and specularly reflected ones. There is reason to believe that the numerical values of these coefficients may depend on the absolute value of the velocity of the incident particles. For this reason, in order to obtain data which can be used in aerodynamic problems, experiments of this type should be conducted with beams whose velocities are as close as possible to the real ones. This can be accomplished, for example, by using the source of fast beams proposed in Ref. 29.

Interesting observations were made in Ref. 159 concerning the regularity of the reflection of a beam of molecular hydrogen from the surface of tungsten. The authors were able to establish the interesting and practically important fact that the nature of the reflection changes with the surface temperature. They found that when the temperature of the reflecting surface is raised to 2200°C, the totally diffuse distribution of the reflected stream is converted into a distribution having a marked directivity, a predominant direction of escape of the reflected particles. This phenomenon took place at lower temperatures (500 to 800°C) for other materials also. Similar effects were also observed by this author (Ref. 157). Thus, a preliminary conclusion which may be drawn from the results discussed above is that the diffuse-specular reflection scheme is inapplicable. Moreover, the investigations showed the necessity of considerable improvement in the vacuum conditions of the experiments.

The exchange of energy between the particles and the surface is described by a quantity (the accommodation coefficient) which is a measure of the adjustment of the average energy of the reflected particles to the value corresponding to the surface temperature. A mathematical expression of this coefficient depends of course on whether the gas is considered

to be moving or stationary, but the numerical value determined by the average amount of energy lost by an individual particle in a collision is included between unity (complete adjustment) and zero (absence of energy exchange). A large number of studies have been devoted to the measurement of this coefficient, and all made use of the "heated" filament method (Ref. 160). A detailed analysis of this method and of the data obtained is given in Refs. 160-162.

However, this method has a number of drawbacks (Ref. 163) which can be overcome by using the MBM.

Two methods of measurement are possible in this case. First, a mechanical selector can be used to study the velocity distribution of the particles reflected from the surface (Ref. 164), and, if the velocities of the incident particles are known, the accommodation coefficient can be calculated. This method, involving the use of an Na beam, made it possible to establish that in the range of 500 to 2000°K, there is a complete accommodation on metallic surfaces (Cu, Al, W, MgO) and an incomplete accommodation of atoms on the crystal surface of LiF ($\alpha = 0.7 \pm 0.1$). /319

In another variant of the use of the MBM (Ref. 163), a monokinetic beam of known velocity is directed at the surface, and the average velocity of the reflected particles is determined from the time of flight. This variant also offers the possibility of a direct measurement of the periods of time during which the molecules stay on the surface, if they are comparable to the time during which the particles travel from the surface to the detector (Ref. 47).

Measurements made by the author showed that for beams of N_2, CO_2, and Ar with an energy of $\sim$1.0 ev, capture takes place on metallic surfaces (Cu, Fe, Ta), and the measured lifetimes of the particles captured on the surface amount to tens (10 to 30) of microseconds.

In addition to having an obvious applied significance, the study of energy exchange between molecules and solids is also interesting as a means of verifying the theoretical concepts of this phenomenon.

The theoretical analysis of this phenomenon, carried out mainly before the 1940's and summarized in a survey article by Frenkel, (Ref. 165) leads to two extreme cases: one, equivalent to an elastic collision of the impinging atom with an individual atom on the surface, and the other, equivalent to an impact excitation of an oscillator approximating the normal vibrations of a crystal lattice. The available experimental data are in poor agreement with the second possibility, and the elastic scheme is confirmed only at very high relative collision energies. Thus, there is a need for improvement of the methods of theoretical description

of this phenomenon, and the main outlines of this improvement are indicated by Frenkel' in the above article.

In particular, one possibility involves the examination of the effect of a collision between an atom or molecule and a linear (or three-dimensional) chain of atoms linked elastically (or otherwise); this being a more adequate model of a solid. The results of such a calculation may give both the energy threshold for the capture of an incident particle, and the dependence of the energy of the reflected particle from the initial energy. An attempt to solve such a problem analytically was made in Refs. 166, 167.

An experimental study of the interaction of chemically active atoms (H, O) with the surface of a solid was carried out with the use of a modulated beam in Refs. 62, 168. In these investigations, the particles reflected from the surface were mass-analyzed; since the ionization cross sections were known, the mass analysis permitted quantitative estimates of the proportion of particles recombining on the surface. In addition, it was possible to estimate the upper limit of the fraction of the dissociation energy carried away by the particles recombining on the surface. In particular, according to Ref. 62, in the case of hydrogen only 3 percent of the energy evolved during recombination is carried away, 97 percent being transferred to the surface.

In Ref. 168, a study was made of the temperature dependence (between 4 and 100°K) of the probability of recombination of atomic hydrogen on the surface of copper. An abrupt increase in the probability of reflection of atomic hydrogen and deuterium was observed at about 4 and 6.5°K, respectively, followed by a steep decline as the temperature decreased. In addition to other factors, an interpretation of these measurements is also rendered difficult by the fact that owing to the condensation of the residual gases, the effective surface changes qualitatively with a change in temperature. A gradual decrease in temperature is accompanied by the formation of successive layers of ice, frozen nitrogen, oxygen, and molecular hydrogen on the surface of copper. Condensation /320
of beams of the molecular gases H_2, N_2, O_2, and H_2O on a surface was also studied (Ref. 168). The use of the MBM offers some enticing possibilities of studying inelastic processes in collisions with surfaces.

At the present time, a focus of major interest is, for example, the study of the deactivation of electron-excited particles on walls. Experimental investigations of this phenomenon can be carried out by using beams shaped from a gas which has passed through a region of high-frequency electrodeless discharge. In this case, the desired information can be obtained by plotting the ionization curves for the direct beam and the beam reflected from the surface.

An inelastic surface process commonly studied by means of the MBM is surface ionization, which is discussed in Refs. 170, 171.

In the problem examined here, the study of the process of an adsorption interaction of the molecules with the surface occupies an important place. However, progress in this field is severely limited by the inadequacy of the traditional methods. The MBM arms the experimenter with a powerful means of investigating this problem--providing him with the theoretically sound possibility of working at the ultimate vacuum, i.e., with surfaces of maximum obtainable purity. Of major interest in this regard are the results of Ref. 169, devoted to the elaboration of a design and creation of an instrument permitting a study of the effects of adsorption interaction in a vacuum of the order of 10^{-10} mm Hg by means of the MBM.

In the last few years, both the techniques of the MBM and the possibilities of its successful application have undergone a considerable expansion. The achievements in the technical field and the results of the application of the method demonstrate the promise of this method and the absolute necessity of including it in the arsenal of experimental means used in solving the problems of molecular physics.

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